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FORMATION OF NUCLEI DURING PRECIPITATION IN METALLIC MIXED CRYSTALS

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16. Abstract

Assuming that the energy of a mixed crystal can be calculated by simple addition of neighboring bonds, the nuclear formation energy is calculated for precipitation in a super-saturated binary mixed crystal. From this can be determined the frequency of the formation of nuclei. From the calculation of a numerical example we can obtain, for the degree of sub-cooling at which the frequency of the formation of nuclei reaches its maximum, satisfactory agreement with available measurements of the rate of precipitation.

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Formation of nuclei during precipitation in metallic mixed crystals* /128**

Assuming that the energy of a mixed crystal can be calculated by simple addition of neighboring bonds, the nuclear formation energy is calculated for precipitation in a super-saturated binary mixed crystal. From this can be determined the frequency of the formation of nuclei. From the calculation of a numerical example we can obtain, for the degree of sub-cooling at which the frequency of the formation of nuclei reaches its maximum, satisfactory agreement with available measurements of the rate of precipitation.

As a rule, the assertions of the accepted theory of thermo-dynamic equilibrium are limited to information relating to the coexistence of different phases. "Water vapor is in equilibrium with liquid water at 100°C and at a pressure of 1 atm." However, this does not say anything about the conditions under which the second phase arises from the original pure phase, We know that pure vapor can be super-saturated, just as pure liquid can be super-heated, without the other phase occurring in time periods on the order of magnitude of hours ordays. In the case of evaporation or condensation, the cause of this delay can be largely explained quantitatively[1)2)]. In the case of condensation it consists of the fact that condensation - excluding wall effects - must first begin with the formation of small droplets of liquid. However, the vapor pressure of these, because of surface tension, is much greater than that of an extended liquid surface. Therefore, compared with very small drops, the vapor is not super-saturated at all, so that a droplet of this kind, even once it has been formed, in general immediately evaporates again. This vapor pressure has a quite definite critical droplet radius at which the droplet is just in (labile) equilibrium. We call this droplet a

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"seed" for the condensation process. Only a seed or nucleus can grow further in the usual sense as a result of condensation. On the other /129
hand, the formation of a nucleus is a typical fluctuating phenomenon associated with the reduction of entropy. A precise analysis[3) 4)] of this phenomenon has shown that the number J of nuclei produced per second is given by

$$J = K e^{-\frac{A}{kT}},$$

(1)

in which A signifies the energy that has to be expended in order to produce a nucleus reversibly and isothermally within the homogeneous phase. The constant K is essentially given by the number of gas-kinetic collisions. With the aid of (1) it was possible to calculate the degrees of over-saturation at which spontaneous vapor formation occurred in the Wilson chamber, producing excellent agreement with experience. A correspondingly complete and quantitative treatment of the super-heating of liquids (formation of vapor bubbles) was recently provided by W. Doering[5)].

An initial attempt will be made in the following to give a quantitative discussion of the formation of nuclei when a binary mixed crystal disintegrates, using a graph of its state as shown in Fig. 1. A and B are the two components, abscissa α is the mole fraction of component A, and the ordinate is the temperature. In the zone above the curve ACB the mixed crystal is stable (point E), but below this curve we are in unstable territory. When E cools via D to E' one would expect a breakdown into the two alloys E" and E"'. In actual fact, however, on observes that this breakdown does not yet occur when the equilibrium temperature T_D is not quite reached. Only at a much lower temperature does the rate of precipitation reach its maximum. When even greater cooling occurs (about F), this rate decreases again to imperceptibly low levels, since now the diffusion rate has become too low (freezing of the state of super-saturation). /130
As typical examples of this behavior we have taken from the literature two different measurements. Figure 2 comes from a study by Johansson and Hagston[6)] in which is plotted the resistance temperature curve of an Au-Pt alloy with 30% platinum. abcd is the equili-

/129

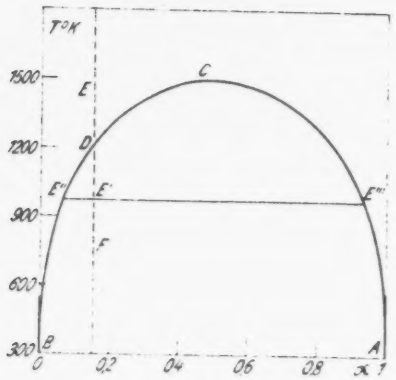

Fig. 1. Graph of the state of a binary mixed crystal.

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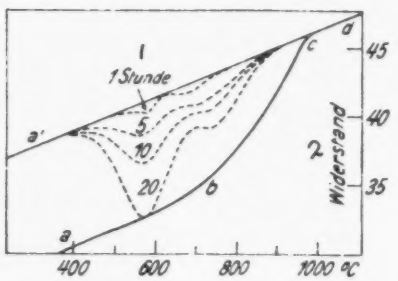

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Fig. 2. Electrical resistance of Au-Pt with 30% Pt acc. to Johansson and Hagsten

Key: 1 1 hour; 2 resistance.

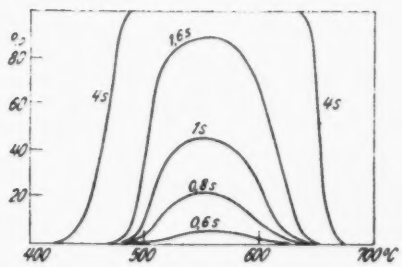

Fig. 3. Austenitic breakdown at different degrees of sub-cooling according to magnetic measurements by H. Lange and H. Haensel.

brium curve as it can be realized with sufficiently slow cooling. /130
The upper part c--d corresponds to the homogeneous mixed crystal; its rectilinear extrapolation, the straight line a'--c--d, represents the resistance of the sub-cooled mixed crystal. The distance a'--a of this straight line from the equilibrium curve is therefore the reduction in resistance caused by the precipitation process. If the mixed crystal is now lowered from point d to a temperature that lies below c and is kept at this temperature for 1, 5 or 10 hours, then one obtains the resistance values that lie on the correspondingly plotted curves. Thus these curves represent a measurement of the rate of precipitation. The latter is very low, just below c, and does not reach its maximum until about T = 740°C; i.e. about 200° below the thermodydnamic conversion temperature of 954°C.

The next figure shows the considerably more complicated process involved in the breakdown of a carbon steel with 1.16% C when it is cooled below the austenitic stability limit, which is about 710°C; the austenite then breaks down into perlite, i.e. a mixture of ferrite and cementite. Ferrite is ferro-magnetic, while austenite is not. In this way it is possible, after reduction to a lower temperature, /131
to follow the chronological increase in the amount precipitated. These types of measurements [7) 8)] produced the the behavior shown in Fig. 3. Here are shown the amounts converted (in %) after certain times, as a function of the sub-cooling temperature. The maximum conversion rate is in this case about 160° below the thermodynamic conversion point.

The reason for the delay in precipitation just below D consists in this case also, as will be shown, in the infrequency of the formation of nuclei. We imagine precipitation in such a way that first of all, within the super-saturated phase produced by E', in a small, more or less cube-shaped area, an accumulation of atoms A takes place as a result of diffusion, corresponding to the point E"' on the graph of the state. We will show that such a cube can only act as a "seed" for further precipitation if the length of its edge exceeds a certain critical measurement. In the presence of smaller cubes, the state E' is not super-saturated at all. Thus any point below D involves a nucleus with a certain edge length

a_0; this nucleus must have formed initially only as a result of fluctuating phenomena, before super-saturation as such becomes effective. a_0 is infinitely large at point D itself and rapidly decreases with increasing sub-cooling. In this case also the surface energy of the nucleus against the surrounding substance plays the critical role. For the frequency of the formation of nuclei we expect an expression similar to expression (1). It should be noted, however, that instead of the constant K, which of course gave the number of gas-kinetic collisions, the frequency of the simple position changes in the solid body now appears. The temperature dependency of this can be measured by observation of the diffusion, which is, of course, only given by the frequency of the position changes. Diffusion can be attributed to an activation heat Q in the sense that the following applies:

$$\text{Diffusion} \approx \text{const} \cdot e^{-\frac{Q}{kT}}$$

In the case of Au-Pt, for example, according to Jost[9]:

$$Q = 39\,000 \text{ cal/Mol.}$$

Thus for the formation of nuclei we now expect /132

$$J = C \cdot e^{-\frac{Q}{kT}} \cdot e^{-\frac{A}{kT}},$$

(2)

in which Q represents a constant that can be taken from diffusion measurements. A is again the nuclear formation energy or also, if volume changes are not involved, the increase in free energy that is associated with the formation of a nucleus. If A is known in relation to T for a certain concentration, then the temperature for the most rapid precipitation is given by the temperature that makes the expression $\frac{Q + A}{kT}$ the minimum. If therefore A is known as a function of T, then the temperature T_K for the most rapid formation of nuclei follows from

$$Q = T\frac{dA}{dT} - A.$$

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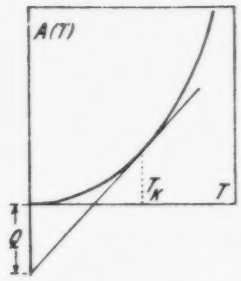

Fig. 4. Diagram for obtaining the temperature for the most frequent formation of nuclei.

Plotted as a graph (Fig. 4) this equation tells us: If one plots on the ordinate axis of a T-A coordinate system the value Q from its origin downwards and draws from the end point of this line the tangent on the A(T) curve, then the contact point supplies the temperature T_K that is being sought. The objective of this study is a quantitative calculation of A and thus of the temperature pattern of I on the basis of a simple and proven theory. This theory was first introduced by Bragg and Williams[10) 11) 12)] for quantitative analysis of the superstructure. It states: Each atom in the crystal is energetically joined only to its Z closest neighbors (Z = 6,8,12 in the simple cubic, cubically space-centered cubically surface-centered lattice). In addition, the bonding energy to a certain neighbor only depends on the nature of the atom itself and of the neighbor; on the other hand, this energy is independent of the composition of the other neighbors. The total bonding energy of the crystal is then simply the sum of all neighboring bonds. It can naturally be expected, and has also been proved, for example, by Borelius[13)], that this picture even in the simple Au-Pt case, which proceeds without any change in the type of lattice, does not entirely do justice quantitatively to the actual behavior. It will /133 be even more difficult to render in this schematic form the more complicated process of the breakdown of austenite. However, it appears to produce very useful results for the qualitative description, relating to orders of magnitude, of certain important processes in solid bodies. In particular, when one accepts the theory of simple neighboring bonds, the calculation of the nuclear formation energy

can be carried out quantitatively using only the numerical data that has essentially already been given by the diagram of the state. /133

The free energy of the homogeneous mixed crystal

The mixed crystal contains in statistical distribution at the temperature T

$N \cdot \alpha$ atoms of type A
$N \cdot (1-\alpha)$ atoms of type B.

Z is the number of neighbors. V_{aa} is the energy of a bond between two A atoms, V_{bb} the energy of a bond between two B atoms and V_{ab} the energy of a bond between A and B. Each A atom has on average $Z\alpha$ neighbors of type A and $Z(1-\alpha)$ neighbors of type B, etc. From this follows for the

number of A-A bonds: $\frac{1}{2} N Z \alpha^2$,
number of B-B bonds: $\frac{1}{2} N Z (1-\alpha)^2$,
number of A-B bonds: $N Z \alpha (1-\alpha)$.

Multiplication of the first line by V_{aa}, the second by V_{bb} and the third by V_{ab} and addition gives the total bonding energy

$$U = NZ\left[V\alpha(1-\alpha) + \frac{1}{2}\bar{V} - \frac{1}{2}V_\delta(1-2\alpha)\right]. \tag{3}$$

In this the following applies:

$$\begin{cases} V = V_{ab} - \frac{1}{2}(V_{aa} + V_{bb}); \\ \bar{V} = \frac{1}{2}(V_{aa} + V_{bb}); \quad V_\delta = \frac{1}{2}(V_{aa} - V_{bb}). \end{cases} \tag{4}$$

For our purposes the summand $\frac{1}{2}\bar{V}$ in (3), which is independent of α, is meaningless. In addition, for simplification we make $V_\delta = 0$ (any difference between V_{aa} and V_{bb} could easily be taken into account if necessary). Accordingly, the decisive factor for everything else is just a value V that is defined by (3) and which tells by how much similar neighbors are more strongly bound to each other than unlike neighbors. We can obtain the entropy S of our mixed crystal from

Boltzmann's equation $S = k \ln W$, /134

in which W gives the number of possibilities for distributing $N\alpha$ A atoms and $N(1-\alpha)$ B atoms over the N lattice positions. This means that

$$W = \frac{N!}{(N\alpha)!\,(N(1-\alpha))!}.$$

Using Stirling's formula $(\ln N! \cong N \ln N)$ we get

$$S = -kN\,(\alpha \ln \alpha + (1-\alpha)\ln(1-\alpha)).$$

(5)

The free energy of the entire crystal is U - TS; i.e. the free energy per atom is

$$f(\alpha) = \frac{U - TS}{N}$$

or

$$f(\alpha) = VZ\alpha(1-\alpha) + kT\,(\alpha \ln \alpha + (1-\alpha)\ln(1-\alpha)).$$

(6)

In Fig. 5 is shown the pattern of $f(\alpha)$ for various values of T. At a given temperature $f(\alpha)$ has two minima α_1 and α_2. One can obtain their values from $\frac{\partial f}{\partial \alpha} = 0$ or

$$\frac{1-2\alpha}{\ln \frac{1-\alpha}{\alpha}} = \frac{kT}{ZV}.$$

(7)

The two roots α_1 and α_2 of (7) that are symmetrical to $\alpha = 0.5$ are close to $\alpha = 0$ and $\alpha = 1$ for low T values. With increasing temperature they move more to the middle. At $\frac{kT}{ZV} = 0.5$ they are both equal to 0.5. If one draws the minima α_1 and α_2 for the $f(\alpha)$ curve as a function of the temperature, then one obtains the diagram of the state shown in Fig. 1. From the temperature at the apex of the unstable zone we can then obtain the numerical /135 value for ZV. For example, for Au-Pt this temperature is 1500°K; i.e. here we get $ZV = 2k \cdot 1500$.

/134

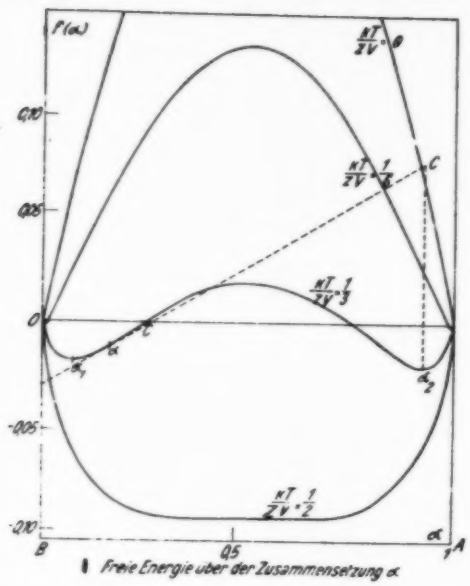

Fig. 5.

Key: 1 Free energy via the synthesis α

The change in free energy when precipitation occurs /135

We will now look closely at the precipitation at the given temperature T and the given concentration α of the A components. α should lie, as indicated in Fig. 5, only slightly above α_1, so that the alloy consists mainly of the metal B. We consider it as a super-saturated solution of A in B. The onset of precipitation consists of a cube-shaped zone forming at any point in the synthesis α_2 as a result of diffusion processes. The length of the edge of the cube is a lattice constant , and thus the cube contains $n = a^3$ atoms. The associated increase F in free energy we break down into two parts

$$F = F_1 + F_2,$$

(8)

of which F_1 is negative, and proportional to the volume of the nucleus. F_1 can be calculated directly from the course of the $f(\alpha)$ curve. F_2 is positive, proportional to the surface of the cube, and is given by the surface energy.

In order to calculate F_1 we now have to take into account the fact that when the cube is precipitated an alloy with N atoms and the concentration α turns into two different alloys, of which one contains n atoms of the composition α_2 and the other contains N - n atoms with the composition α'. The value of α' is obtained from the constancy of the total number of A atoms:

$$N\alpha = (N-n)\alpha' + n\alpha_2$$

or

$$\alpha - \alpha' = \frac{n(\alpha_2 - \alpha)}{N-n}.$$

For the increase in free energy we thus obtain

$$F_1 = n f(\alpha_2) + (N-n) f(\alpha') - N f(\alpha).$$

Since N >> n, α - α' will be a small number. Therefore we can say:

$$f(\alpha') = f(\alpha) - \frac{df}{d\alpha}(\alpha - \alpha').$$

Using the above value for α - α' we therefore get:

$$F_1 = -n\left[f(\alpha) - f(\alpha_2) + f'(\alpha)[\alpha_2 - \alpha]\right].$$

(9)

The expression in parentheses has a simple geometric significance. /136
If one brings (in Fig. 5) to intersection C the tangent drawn at the point α on the $f(\alpha)$ curve using the parallels to the ordinate axis drawn through α_1, then

$$f(\alpha) - f(\alpha_2) + f'(\alpha)(\alpha_2 - \alpha)$$

is equal to the rise C - $\bar{\alpha}_2$ of the point C above the $f(\alpha)$ curve at the point α_2. From this construction one can see immediately that in the alloy that is richer in B, nuclei can only be formed on the side lower in B. The formation of a cube with the composition α_1 would always be associated with an increase in free energy.

(9) gives the increase in F for the case in which n atoms of the composition α precipitate without new interfaces being formed. Thus (9) refers to the case in which the phases α and α_2 adjoin each other with a large flat surface and phase α_2 increases by n atoms when the interfacing plane shifts, while at the same time there is a homogeneous reduction in phase α. In order to produce

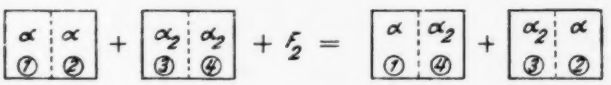

Fig. 6. Diagram for calculation of the surface energy.

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a cube of α_2 embedded in α we can now proceed in such a way that we extract from each of the phases α and α_2 a cube with the edge length a and exchange these two cubes. The volume of the phases α and α_2 is not changed, but twice the surface of the cube is produced (interfacing surface α versus α_2). From this hypothesis is produced the following scheme for calculating the surface energy for a cube with s surface atoms (in a simple cubic arrangement, $s = 6\ a^2$): One takes (Fig. 6) one block each from phases α and α_2 with a cross section $\frac{1}{2}$ s and divides one into parts 1 and 2 and the other into parts 3 and 4. Then one puts the partial blocks together again cross-wise (1 with 4 and 3 with 2), so that one gets twice the surface s/2 at interface α_2 versus α. We have to calculate the energy F_2 which has to be expended in total in this process. F_2 is equal to the increase in the bonding energy that goes beyond the dotted interface. We calculate using a simple cubic arrangement. Now the s/2 bonds consist in the case of the α- α blocks of the components $\alpha^2, (1-\alpha)^2, 2\alpha(1-\alpha)$ from A-A, B-B and A-B bonds. The corresponding components in the case of the blocks put together out of α and α_2 are /137

$$\alpha\alpha_2,\ (1-\alpha)(1-\alpha_2) \quad \text{and} \quad \alpha(1-\alpha_2)+\alpha_2(1-\alpha).$$

Thus we have

$$\begin{aligned} F_2 = \frac{s}{2}\big[&2\alpha\alpha_2 V_{aa} + 2(1-\alpha)(1-\alpha_2)V_{bb} + 2\left(\alpha(1-\alpha_2)+\alpha_2(1-\alpha)\right)V_{ab} \\ &-\alpha^2 V_{aa} \quad -(1-\alpha)^2 V_{bb} \quad -2\alpha(1-\alpha)V_{ab} \\ &-\alpha_2^2 V_{aa} \quad -(1-\alpha_2)^2 V_{bb} \quad -2\alpha_2(1-\alpha_2)V_{ab}\big]. \end{aligned}$$

The final calculation gives simply

(10) $$F_2 = s\,V(\alpha-\alpha_2)^2,$$

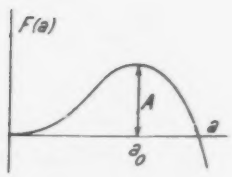

Fig. 7. The energy F(a) that has to be expended to produce a cube with the side length a

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in which

$$V = V_{ab} - \frac{1}{2}(V_{aa} + V_{bb})$$

signifies the value already introduced in (4).

Using the side length a for our cube measured in lattice constants, in (9) we get $n = a^3$ and in (10) we get $s = 6\,a^2$, so that according to (8) altogether the formation of this cube is associated with the increase in free energy

$$F = -a^3[f(\alpha) - f(\alpha_2) + f'(\alpha)(\alpha_2 - \alpha)] + 6a^2 V(\alpha - \alpha_2)^2$$

(11)

As a function of a, F has the pattern shown diagrammatically in Fig. 7. F increases with increasing a to a maximum value A at the side length a_0. This a_0 is the side length of the nucleus, and A is the nuclear formation energy. A cube with the side length a_0 may grow as the free energy decreases, while a smaller cube generally becomes dissolved again. According to (11) a_0 follows from $\frac{\partial F}{\partial a} = 0$ to

$$a_0 = \frac{4V(\alpha - \alpha_2)^2}{f(\alpha) - f(\alpha_2) + f'(\alpha)(\alpha - \alpha_2)}$$

(12)

and thus $A = F(a_0)$ or

$$A = 2a_0^2 V(\alpha - \alpha_2)^2.$$

(13)

Calculation of a special example

/138

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Table 1

α_1	α_2	ϑ	T	a_0	A cal/Mol	$\frac{A+39000}{RT}$	$e^{-\frac{A+39000}{RT}}$	$\frac{A+20000}{RT}$	$e^{-\frac{A+20000}{RT}}$
0,15	0,85	0,404	1211	∞	∞	∞	0	∞	0
0,10	0,90	0,364	1092	7,0	55200	43,4	$1,35 \cdot 10^{-19}$	34,6	$8,15 \cdot 10^{-16}$
0,08	0,92	0,344	1032	4,7	26100	31,7	$1,59 \cdot 10^{-14}$	22,5	$1,69 \cdot 10^{-10}$
0,06	0,94	0,320	959	3,4	14100	27,9	$7,76 \cdot 10^{-13}$	17,9	$1,66 \cdot 10^{-8}$
0,05	0,95	0,306	917	2,9	10600	27,3	$1,45 \cdot 10^{-12}$	16,8	$4,94 \cdot 10^{-8}$
0,04	0,96	0,290	868	2,5	8100	27,3	$1,38 \cdot 10^{-12}$	16,3	$8,41 \cdot 10^{-8}$
0,03	0,97	0,270	811	2,1	6100	28,0	$6,86 \cdot 10^{-13}$	16,2	$9,07 \cdot 10^{-8}$
0,02	0,98	0,247	740	1,8	4500	29,5	$1,42 \cdot 10^{-13}$	16,6	$5,85 \cdot 10^{-8}$
0,01	0,99	0,213	640	1,5	3100	33,1	$4,08 \cdot 10^{-15}$	18,2	$1,27 \cdot 10^{-8}$

We will look in particular at the case of an alloy in which the miscibility gap closes at 1500° K and for which the activation heat Q for the position change is 39,000 g cal/mol. Insofar as it is possible to look at the alloy using the idea of the simple neighboring exchange effect, these data are sufficient not only to calculate the precipitation curve (diagram of the state) but also to calculate the relative rate of the formation of nuclei in the subcooled state. We assume a simple cubic lattice and thus assume Z = 6. First of all follows from the figure of 1500°:

$$\frac{R\,1500}{Z\,V} = 0{,}5$$

or Z V = 3000 g cal/mol. If we also use for brevity the designation

$$\vartheta = \frac{R\,T}{Z\,V},$$

then we get from (7) the values for ϑ and T = 3000 ϑ in the diagram of the state that apply to the two points α_1 and $\alpha_2 = 1 - \alpha_1$, as is shown in columns 3 and 4 of Tab. 1. The other columns in the table are related specifically to the case of an alloy with $\alpha = 0.15$, i.e. 15% of the components capable of being precipitated. As a mixed crystal it is unstable at temperatures below 1211° K. The other columns in the table give the values that apply at different temperatures for a_0, A, and $\frac{Q + A}{kT}$ as well as, finally, the

relative rate of nuclear formation $e^{-\frac{Q+A}{kT}}$. . The latter values are given once using the value Q = 39,000 cal/mol taken from diffusion measurements with Au-Pt and again using the value Q = 20,000 cal/ /139
mol, which is about half as great. The figures calculated are rendered graphically in Fig. 8 in such a way that, in addition to the curve for A9T), the values J/J_{max} are plotted. If one compares these curves with the experimental precipitation curves in Figs. 2 and 3, one is struck by the fact that the greatest rate of nuclear formation (at Q = 39,000) occurs at about 300° below the conversion temperature. This order of magnitude agrees satisfactorily, within the scope of this whole discussion, with the corresponding values for the measured maximum precipitation rate shown in Fig. 2, in which the first maximum on the curve measured after about 1 hour lies 250°C below c.

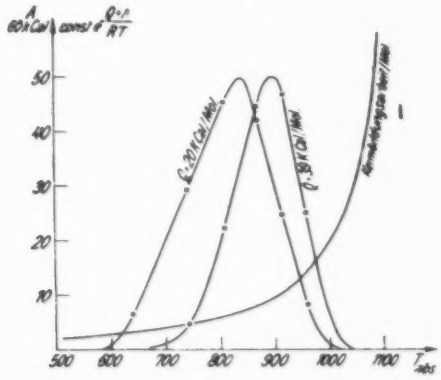

Fig. 8. ----- : Relative rate of nuclear formation using two different values for the activation heat Q of the diffusion.

Key: 1 nuclear formation energy

Incidentally, it should be emphasized that in Figs. 2 and 3 the precipitated amounts were measured, while in Fig. 8 the rate of nuclear formation expected at the onset of precipitation was calculated. A difference between volume curves (2,3) and the nuclear formation curve (8) is significant for two reasons. First of all,

the nuclei that are formed at different times will have grown by a certain later time to different sized crystallites*, and so then, as the precipitation progresses, the remaining mixed crystal will constantly approach in concentration the equilibrium value α_1. However, this means that the nuclear formation energy constantly increases. A comparison of curve 8 with the experimental curves in Fig. 2 is therefore permissible at the most at the onset of the process. A /140
look at the Au-Pt resistance curves in Fig. 2, which obviously show two maxima, then leads one to assume that two processes may overlap here; these can possibly be interpreted by means of two different values for Q, of which the higher value (about 39,000) might belong to the position change within the crystallite, while the smaller might belong to the position change processes on the more disturbed crystallite edges. This interpretation could possibly be tested by means of metallographic analyses of the photomicrographs of the Pt precipitation that takes place above 700°C and below 600°C. At lower temperatures the crystallite edges would have to be favored in the precipitation process, while at higher temperatures this process would have to take place homogeneously throughout the entire crystallite.

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* If one assumes that the nuclei, once they have formed, grow at an exp. $\left(-\frac{Q}{kT}\right)$ proportional, constant, linear rate, then to the exponent $\frac{(A + Q)}{kT}$ in the nuclear formation rule would belong an exponent $\frac{(A + 4Q)}{kT}$ for the amount precipitated in the initial stage of the process.

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